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The nuclear magnetic moments of D^2, Li^7, and F^{19} studied by the magnetic resonance absorption method

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With 13 figures in the text

Introduction

When the magnetic resonance principle was applied to molecular beams by RABI and co-workers a very high degree of precision was made possible in the determination of nuclear magnetic moments. This method and some of the most important results obtained with it have recently been the subject of a survey[1] and will not be discussed here. It is sufficient to mention that the precision in the value of the magnetic moments are given with an accuracy of roughly 0.5–1 ‰. The limitation in precision is mostly due to the natural line-widths obtainable and though, at least in principle, this limitation could be made less pronounced by using a longer C-magnet this would involve rather great practical difficulties.

A considerable increase in the definition of the resonance lines was made possible by the new methods of PURCELL, TORREY and POUND[2] and BLOCH, HANSEN and PACKARD[3]. The two methods, put forward simultaneously and independently of each other, are rather similar in principle, the difference being well described by the names of the two methods: "Nuclear Magnetic Resonance Absorption" and "Nuclear Induction" respectively. One of the great advantages with these new methods is, of course, that the experimental technique is somewhat easier than the molecular beam method. The most important and promising feature, however, is the extremely small natural line-widths which can be obtained under certain circumstances. This problem is intimately connected with the interesting questions about the relaxation time of the energy exchange between the nuclear spin system and its surroundings. For solids, the statistical orientation of neighbouring nuclear magnetic dipoles will in most cases strongly limit the sharpness of the resonance but, for gases and liquids with suitable relaxation times, one may hope for very much sharper lines than before. Several of these questions have lately been systematically investigated by PURCELL and his co-workers.[4, 5]. In a liquid such as water, all local fields acting on a proton cancel out in a time comparable to a Larmor period due to molecular motion. One therefore gets a lowest value for the expected natural line-width simply by combining the uncertainty principle (1) with the resonance condition (2):

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[1] J. KELLOG and S. MILLMAN, Rev. of Mod. Physics, *18*, 323, 1946.

[2] E. PURCELL, H. TORREY and R. POUND, Phys. Rev. *69*, 37, 1946.

[3] F. BLOCH, W. HANSEN and M. PACKARD, Phys. Rev. *69*, 127, 1946.

[4] N. BLOEMBERGEN, E. PURCELL and R. POUND, Phys. Rev. *73*, 679, 1947.

[5] N. BLOEMBERGEN, Nuclear Magnetic Relaxation, Thesis, Utrecht 1948.

$$\Delta E \cdot \Delta t \sim h \tag{1}$$

$$h\nu = \frac{\mu H}{I} \tag{2}$$

The line-width ΔH will then be

$$\Delta H \sim \frac{H}{\nu \cdot \Delta t} \tag{3}$$

H is the magnetic field when resonance takes place. ν is the frequency of the applied high frequency field and Δt the relaxation time. μ is the nuclear magnetic moment. Δt is ~ 3 sec. for protons in water. H/ν is about $7\,000/3 \times 10^7$. One gets

$$\Delta H \sim 10^{-4} \text{ Gauss}$$

$$\text{or } \frac{\Delta H}{H} \sim 10^{-8}$$

This extremely small value for the relative natural line-width is evidently far too small to be realized experimentally. The limiting factor in such cases will always be the homogeneity of the magnetic field, which of course will introduce a broadening of the line roughly equal to the inhomogeneity of the field on the area occupied by the probe (usually of the order of 1–3 cm^2).

Since the nuclear magnetic resonance absorption is a very small effect because of the small difference in population of the neighbouring magnetic sublevels, it is necessary for that reason also to make all possible arrangements by sacrificing field homogeneity to get high absorption peaks. Any inhomogeneity will spread out the resonance line over a more or less extended area making the signal less observable in the background of noise in the amplifier.

Beyond some fundamental investigations of line-widths and relaxation phenomena by PURCELL's group[1] (loc. cit.) and by BITTER et al.[2] and ROLLIN[3] (the last two groups working also with very low temperatures), the new method has hitherto mainly been applied for precise determination of the magnetic moments of the lightest nuclei, e. g., the neutron,[4, 5] deuteron[4, 6, 7, 8], and triton[9, 10], all compared to the proton.

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[1] It might also be mentioned that the rôle of the electric quadrupole moment of the nucleus in resonance absorption experiments has been investigated by R. Pound (Phys. Rev. *72*, 1273, 1947). Fine structure of the proton resonance line in crystals has been found by G. PAGE (Journal of Chem. Phys. *16*, 327, 1948).

[2] F. BITTER, N. L. ALPERT, H. L. POSS, C. G. LEHR and S. T. LIN, Phys. Rev. *71*, 738, 1947.

[3] B. V. ROLLIN and J. HUTTON, Nature *159*, 436, 1947.

[4] W. R. ARNOLD and A. ROBERTS, Phys. Rev. *70*, 766, 1946.

[5] F. BLOCH, D. NICODEMUS and H. H. STAUB, Phys. Rev. *74*, 1025, 1948.

[6] A. ROBERTS, Phys. Rev. *72*, 979, 1947.

[7] F. BLOCH, E. C. LEVINTHAL and M. E. PACKARD, Phys. Rev. *72*, 1125, 1947.

[8] F. BITTER, N. L. ALPERT, D. E. NAGLE and H. L. POSS, Phys. Rev. *72*, 1271, 1947.

[9] H. L. ANDERSON and A. NOVICK, Phys. Rev. *71*, 372, 1947.

[10] F. BLOCH, A. C. GRAVES, M. PACKARD and R. W. SPENCE, Phys. Rev. *71*, 551, 1947.

He^3 has also recently been investigated[1] but, as the signal to noise ratio in that case was small because of the very small amounts of He^3 available, the magnetic moment in this case could not be determined as accurately as the others. POUND[2] has developed an automatically recording magnetic moment "spectrometer", in which the magnetic field is kept fairly constant during a long time and the high frequency changes slowly and continuously. This device is very convenient and especially suitable when searching for magnetic resonance lines either not known at all before or only very roughly.

In the present paper an apparatus is described for precise measurement of magnetic moments according to the new resonance absorption principles. Emphasizing the importance of the field homogeneity, special attention has been paid to this problem. The homogeneity finally obtained in the rather moderate-sized magnet was sufficient to enable the use of *two* rather big probes simultaneously in the field at different places, so that different samples could be compared to a standard water probe in one of the probe coils. Partly as a check of the apparatus but also because of its special interest, the magnetic moment of the deuteron was first redetermined. It was found that the reproducibility of the individual measurements was as good as could be hoped for from the line-width, provided the signal was made sufficiently strong. Furthermore no systematic errors could be found when the magnetic field was changed appreciably. This apparatus is designed for use in making precise measurements of a number of different nuclei and the first results of these investigations will be given in this paper, namely the magnetic moments of D^2, Li^7 and F^{19}. The sensitivity of the signal detection system used in these investigations still leaves room for improvement and the new arrangements which are under way for this purpose will be described on a later occasion.

The signal detector system

The signal produced when nuclear resonance absorption takes place is of course extremely weak and except in a few cases, such as for protons in water, this difficulty produces rather serious practical limitations of the applicability of the method, which can be overcome only by very careful trimming of the whole detection system. Several suggestions regarding different detectors have been made, among which can be mentioned the balanced high frequency bridge put forward by PURCELL et al.[3], the nuclear induction method[4, 5], the super-regenerative circuit and the autodyne detector, the two last mentioned proposed by A. ROBERTS.[6] All these detectors may have different advantages, depending on the problem which the apparatus will be used for. For our purpose the high frequency bridge ought to be most suitable. The signals are generally rather easy to interpret and the method is almost certainly the most sensitive. It is probably not so easy to handle and adjust as some of the others, especially when a change of the frequency is wanted.

The high frequency balance principle here adopted is illustrated in the block diagram of Fig. 1 and is similar to that described by Purcell et al. (loc. cit.). The

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[1] H. L. ANDERSON and A. NOVICK, Phys. Rev. *73*, 919, 1948.

[2] R. POUND, Phys. Rev. *72*, 527, 1947.

[3] E. M. PURCELL, H. C. TORREY and R. V. POUND, Phys. Rev. *69*, 37, 1946.

[4] F. BLOCH, Phys. Rev. *70*, 460, 1947.

[5] F. BLOCH, W. W. HANSEN and M. PACKARD, Phys. Rev. *70*, 474, 1947.

[6] A. ROBERTS, Rev. Scient. Instr., *18*, 845, 1947.

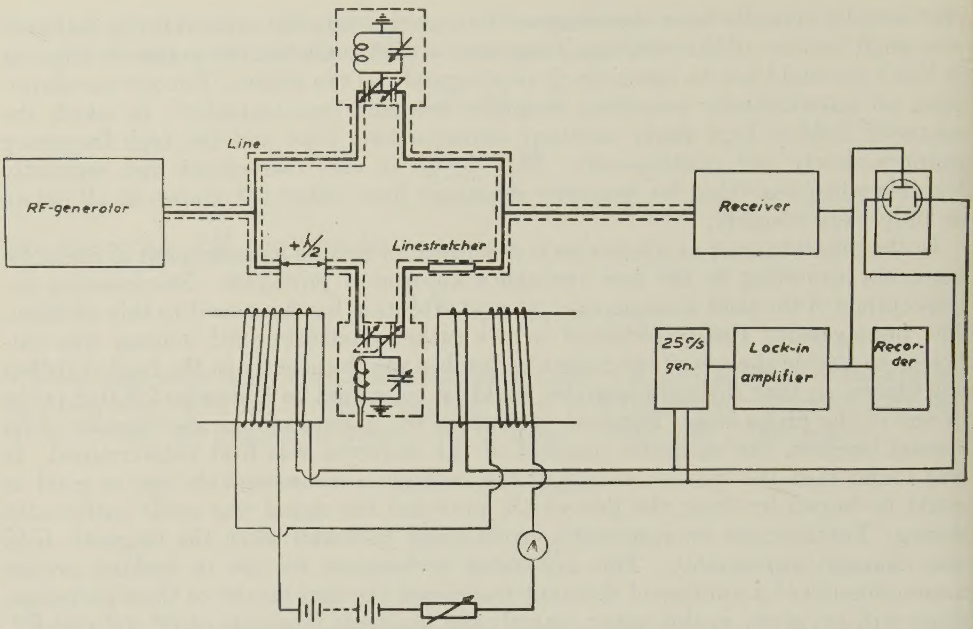

Fig. 1. General principle of the arrangement.

generator feeds a high frequency bridge, which can be balanced both for amplitude and phase. For this purpose one of the two coaxial lines may be made $\frac{\lambda}{2}$ longer than the other, final adjustments being performed with a line stretcher. Moreover the balancing is perfected by means of the coupling condensers of the two band pass filters.

If the frequency is relatively low, say 5 Mc, a phase shift of 180° would introduce an inconveniently long $\frac{\lambda}{2}$ coaxial line (about 20 m). In such cases we have sometimes found it better to use a high frequency transformer with a center grounded secondary winding.

The receivers used in our experiments are of ordinary communication types (National HRO 5 A and Hammarlund HQ 129 X) but the stability of their DC supplies is not sufficiently good for this kind of measurement. We have therefore built special stabilized DC supplies for these receivers and also rebuilt the low frequency parts of them to match them to the oscillograph. This is of a double beam type, so that two different signals can be studied simultaneously on the screen. The sweep can be syncronized by the 25 c/s generator or can be taken directly from a pick-up coil in the magnetic field. As an alternative to the oscillograph, the amplified and rectified signal can also be fed to a phase sensitive lock in amplifier[1] with a narrow band-width around 25 c/s. It can also be fed through an amplifier which is matched to an automatic recorder (Easterline Angus 1 mA).

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[1] R. DICKE, Rev. Scient. Instr., *17*, 268, 1946.

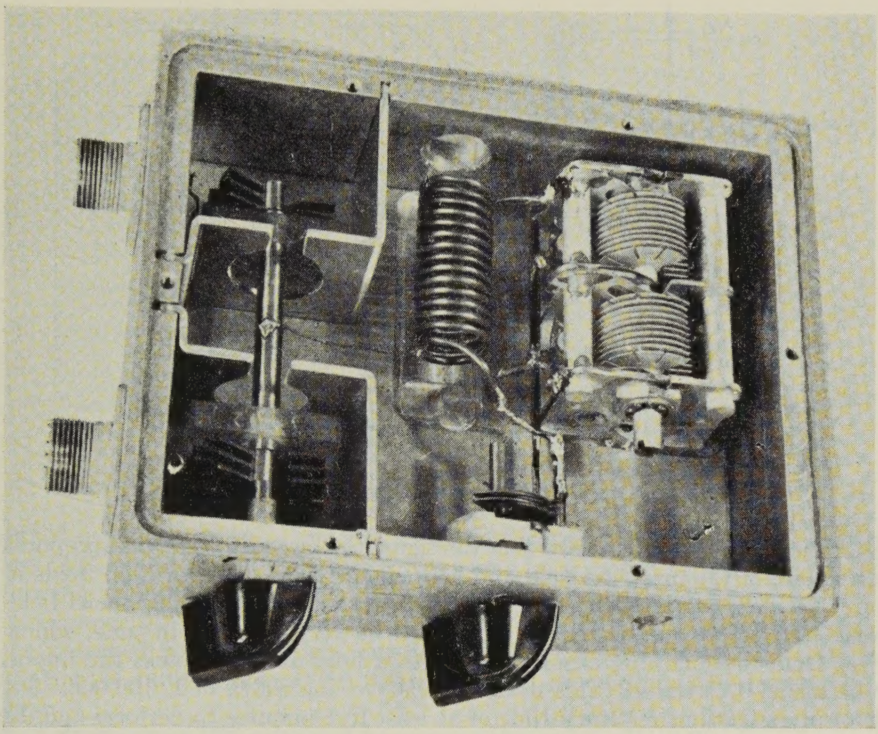

Fig. 2. Filter used in the experiments.

Provided the field homogeneity is sufficiently good many advantages can be obtained by using a big probe coil in the band pass filter. This will increase both the amount of substance which can be put into the coil and also the Q-value of the filter, both of which will increase the signal to noise ratio. Not only the field inhomogeneity but also the space available between the pole pieces will limit these possibilities rather soon, since the Q-value of the coil will drop rapidly when the capacitance to earth becomes important. All these factors make it necessary to make a compromise in the design of the band pass filters. We have made a number of different designs and have tried to reach optimum conditions.

Fig. 2 shows one of the filters used.

The Q-value of the filter is about 100 and has been separately determined, according to Fig. 3.

The coil consists of a copper winding (2 mm thick) with an internal diameter of 12 mm and a length of 30 mm. The cylindrical glass-tube containing the sample can easily be inserted and exchanged in the coil through a hole in the filter box.

The rather big coils and samples which are used in our experiments require correspondingly stronger signal strength from the generators. The adjustments for balancing the bridge are therefore more critical and we have found it necessary to pay some attention to the mechanical stability of the filters, which are made for rather strong performance, as can be seen from Fig. 2.

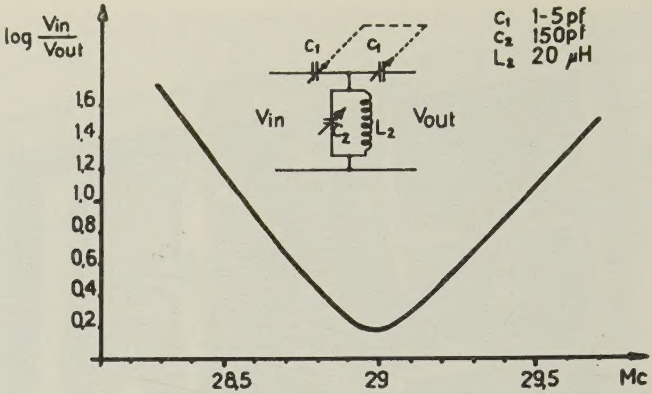

Fig. 3. Characteristic curve for one of the filters used.

The magnet

Theoretical considerations show that the signal to noise ratio is almost proportional to the square of the magnetic field and consequently the need for high fields is obvious. The great importance of an extended and especially homogeneous field has been stressed before. Moreover the field must be very constant in time, which will be clear from the following arguments. With a field of 7 000 Gauss the line-width may be about 0.15 Gauss. This means a relative line-width of 2 : 100 000. Several kinds of investigations require a time of at least five minutes to perform and during this time one should not allow the resonance line to drift more than at the most one line-width. In our investigations the time axis on the oscilloscope often corresponded to less than 0.5 Gauss. A drift of only 0.1% would therefore not merely change the position of the line but would remove it completely from the screen.

For some investigations, a permanent magnet would be convenient[1], e. g., when fine structure or relaxation phenomena of one single resonance line are being studied for a long time. Obviously this type of magnet is less suitable if the magnetic field has often to be changed and especially if the field has to be changed continuously and slowly over rather great intervals when looking for new resonance lines. An electromagnet is therefore the most flexible type. Considering the need for high fields and homogeneity a big cyclotron magnet, if available, could be useful. The generator has to be specially well stabilized, in fact much better than should be necessary for ordinary cyclotron running. Instead, we have reconstructed a moderately sized magnet[2] which is now strongly water cooled and excited by large batteries and moreover fulfils all possible requirements of field homogeneity on a sufficiently large area for our purposes.

A section of the magnet is shown in Fig. 4 (compare also Fig. 9).

The total weight of the magnet is about 1 ton. The airgap can be varied by means of a threaded ring which is provided with handles. It is excited by two water-cooled coils, each made in two sections. The total number of turns is 504 and the copper wire has an area of 2.5 × 3.5 mm. Total resistance is 2.8 ohm. There are two well-

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[1] See G. Pake, Journ. of Chem. Physics, *16*, 327, 1948.

[2] K. Siegbahn, Ark. f. Mat., Astr. o. Fysik, *30 A*, N:o 20, 1944.

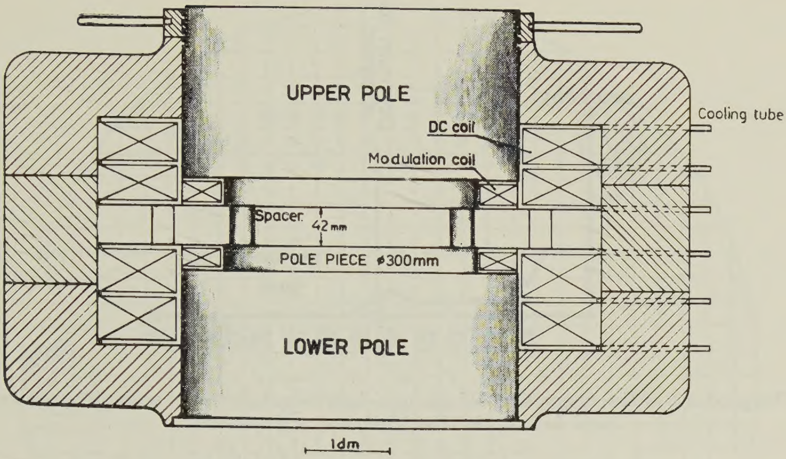

Fig. 4. Cross-section of the magnet (comp. Fig. 9).

machined pole pieces (⌀ = 30 cm) which are separated by three copper bronze spacers, 4.2 cm long. The pole pieces can easily be removed or inserted. Two field modulating coils surround the pole pieces. They contain together 8 000 turns 0.4 mm copper wire, and the total resistance is 1 000 ohm. A modulation of 5 Gauss can be obtained with the 25 c/s generator with an output voltage of 5 volts. The modulation is sinusoidal and the amplitude can be continuously decreased down to zero.

The battery gives 190 volts and has a capacity of 300 a/h at 30 amp. It can give a maximum current of about 70 amp., and the emf at 30 amp. is almost constant for the first few hours.

10 000 Gauss is obtained when the current is 33 amp. which means a power of 3 kW. The temperature equilibrium in the coils can be controlled by several thermometers at different places on the coils. If the current is allowed to excite the coils without cooling for a certain time, the equilibrium after the cooling is turned on can be obtained in less than an hour.

The pole pieces were first given an ordinary machining and the homogeneity was then measured by means of a search coil and a fluxmeter, both along different diameters and in circles around the center. An inhomogeneity of $3:10^5$ could be observed with this arrangement. In this way it was found that one asymmetrically situated place in the field had a high degree of homogeneity. In Fig. 5 the gradient along a diameter and passing through the homogeneous place is given. Incidentally the small hump in the curve at the center is due to the unavoidable smaller grinding speed of the machine there.

The gradient of the homogeneous place in Fig. 5 was then investigated in directions at right angles to the diameter. Unfortunately it was found that the gradient in this direction was less favourable. The actual line-width obtainable with this field was then investigated, using a water probe which in this case was 30 × 7 mm. In accordance with the field measurements the proton resonance line was very sharp only when the probe was put in the homogeneous place and with its axis very nearly along the diameter. If the probe was turned 90° or moved to other places in the field, the line became much broader or even disappeared almost completely.

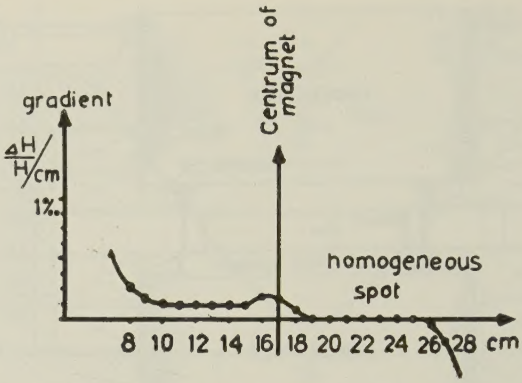

Fig. 5. The gradient of the magnetic field along a diameter, before the pole pieces were polished and before the final magnet adjustments.

For many purposes it would have been sufficient to use this field as it was, if all investigations were limited to the small homogeneous spot. The experimental arrangement planned by us, however, required at least *two*, if possible bigger homogeneous areas, so that two different probes could be investigated simultaneously at some distance from each other. It was therefore necessary to shape the field better.

The pole pieces were removed and the distance between the upper and lower poles themselves was carefully adjusted to be the same in less than 0.01 mm. This was accomplished by inserting very thin iron sheets in the dismountable outer yoke. The two pole pieces were then made *optically flat* and parallel within 1 μ over their whole surfaces by polishing. The spacers were also prepared in the same way.

The field obtained after this treatment is shown in Fig. 6.

The search coil has been moved in directions at right angles to each other. The numbers indicate the differences in field between two points 1 cm apart. The number 1 is a gradient of about $3 : 10^5$, being the smallest gradient which could be measured with any certainty. The number $^1/_2$ is not very significant but indicates only that the fluxmeter made a very small deflection.

The homogeneity of the field is appreciably better now and actually sufficiently good to permit the realization of the two probe arrangements with bigger coils. By means of the water probe, two very good places were located in the area indicated in the figure and situated about 3.5 cm apart, which were used in our final experimental arrangement (see below). When the probes had the dimension 15×30 mm the line-widths were about 2 : 100 000. Considering the great precautions taken in shaping the field and the very small gradients here involved, it is questionable whether one can hope for much better homogeneity with a magnet of a size that can be excited by batteries. Moreover the iron in the pole pieces will probably always contain some internal inhomogeneities which may easily introduce field inhomogeneities of the order of 1 : 100 000. A very much larger magnet or a system of ironless coils designed for highest possible homogeneity could, at least in principle, be expected to produce even smaller line-widths. The practical difficulties of the problem of stabilisation of the generator current, since much higher powers have to be used, should however be considered.

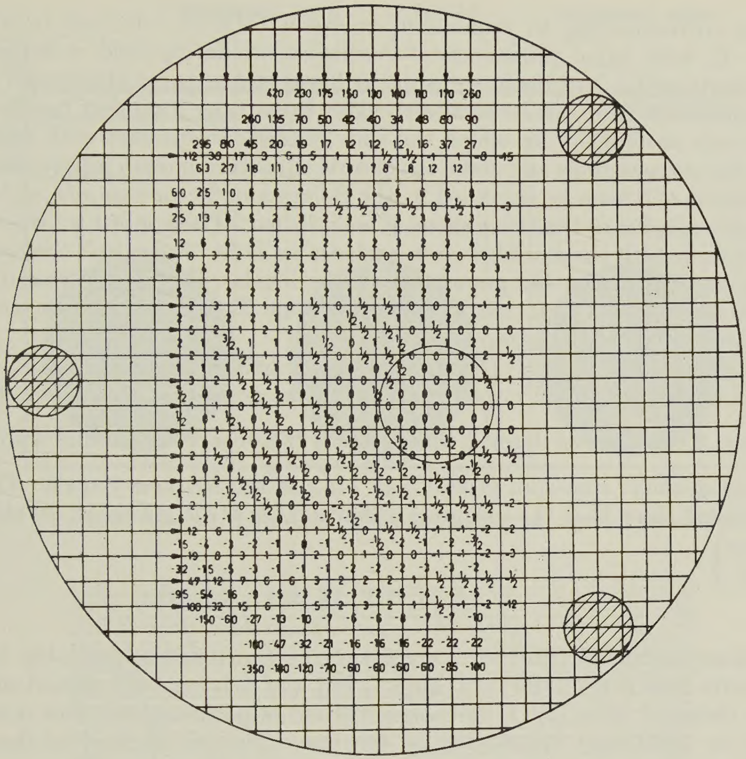

Fig. 6. Gradient map of the magnetic field, after the pole pieces have been made optically flat and the magnet carefully adjusted.

The amount of iron put into the yoke is sufficient to give an almost completely linear relationship between current and magnetic field up to 10 000 Gauss, which makes it easy to locate different resonance lines.

The signal

When magnetic resonance takes place in the sample the signal produced and observed is dependent on a great number of physical and chemical parameters. It is not intended here to give a survey of this complex field which has been and is still being explored, especially by Purcell and Bloch and their co-workers (for references see pages 2 and 5). Only a very brief summary will be given here, sufficient to stress some points of special importance for the realization of resonance lines suitable for precise measurements. The two main requirements are: High peak to noise ratio and small line-width.

The energy levels of a nuclear spin system are characterized by the maximum Z-component of the angular momentum $I\hbar$ and the magnetic moment μ. One can distinguish between $2I+1$ levels spaced in energy by $\mu H_0/I$, where H_0 is the magnetic field at the nucleus. The state of this system can be described in the usual way by the magnetic quantum numbers m_1, $m_2 \ldots$ where $I \geq m_i \geq -I$. There will be transitions corresponding to stimulated emission ($\Delta m = +1$) and to absorption ($\Delta m = -1$), with equal probability if a suitable oscillating field is superimposed.

If one starts with a surplus of spins in the lower states, a net absorption of energy from the radiation field can be obtained. This important condition can be attained if there is any mechanism by which the spin system can interact with and transfer energy to the surroundings and come to thermal equilibrium (spin lattice interaction). The population will then be governed by the Boltzmann factor $\exp(\mu H_0 m_i / I k T)$ and the necessary surplus in the lower states is established. The applied h f field tends by absorption to disturb the equilibrium in such a way as to "warm up" the spin system and bring equivalence in the population of the levels. The spin lattice interaction can be described by a characteristic relaxation time T_1 which has been measured in several cases by Purcell's group.

If the driving signal field H_1 (H_1 defined as one half of the amplitude) is made too strong, de equivalisation in population may be so great that saturation will occur. A quantity T_2^* can be so defined that $\frac{1}{\pi T_2^*}$ is the observed half line-width (due to field inhomogeneity, spin-spin interactions etc.) in the frequency scale. Theoretical considerations[1] show that the optimum condition for H_1 is governed by the relation $\left(\gamma = \frac{2\pi\mu}{I h}\right)$:

$$(\gamma H_1)^2 T_1 T_2^* = 1 \tag{4}$$

The relaxation time T_1 can for convenience be shortened appreciably by adding paramagnetic ions (Cu^{++}, Fe^{+++}, Mn^{++}) but the driving field should not exceed the value obtained from (4). If the concentration of paramagnetic ions is very large there will be additional broadening of the line. Also an increase of the viscosity or a lowering of the temperature will finally increase the line-width.

For precise measurements, liquids (or gases) are of course most suitable, since in these cases the action of the "local" fields from neighbouring nuclei cancel out, which otherwise (as in crystals) gives rise to a rather pronounced broadening of the line (of the order of 10 Gauss).

Naturally the sample chosen should contain as many nuclei per cm^3 as possible, the effect being proportional to the total number of nuclei present.

The signal produced on the fluorescence screen at resonance can be of two different types or a mixture of the two. If the h f bridge is set for unbalance in amplitude, an absorption line is obtained; if it is set for unbalance in phase, one gets a dispersion curve. All other settings give mixtures. For a precise comparison of the location of two different signals on the screen, especially when the signals are so small as to be comparable to noise background, great care has to be taken to get the same type of curve for both signals. Otherwise the maximum, for instance, of one pure or mixed dispersion curve might erroneously be located against the maximum of the other pure absorption line. An error of about one half of the line-width can in that way easily be made for small signals. Under certain circumstances "wiggles" can appear after the true resonance maximum is passed and this may complicate the line interpretation.

The absorption line will generally split up in two on the oscilloscope screen due to the sine modulation of the magnetic field. The splitting up and also the line-width behave in a characteristic manner when the magnetic field is slowly increased, which

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[1] N. Bloembergen, E. Purcell and R. Pound, Phys. Rev. *73*, 679, 1947.

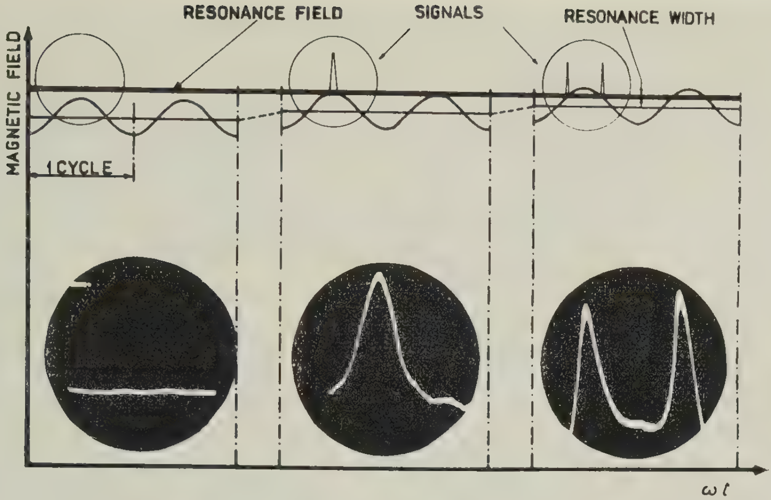

Fig. 7. The behaviour of the proton resonance signal in the sine modulated field.

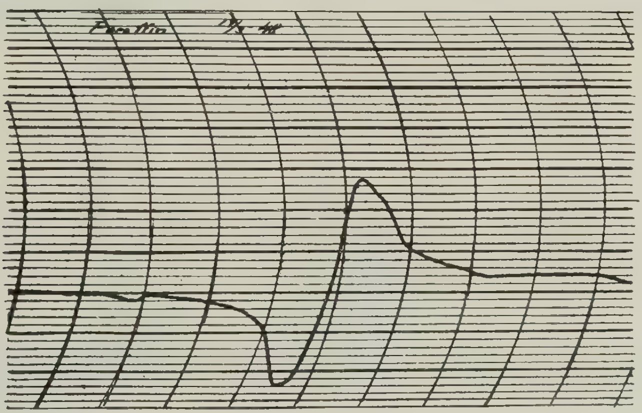

Fig. 8. Resonance curve of dispersion type, registered with the recording Ma-meter.

is illustrated in Fig. 7 showing the proton resonance. If the constant field is so low that the maximum of the superimposed sine wave cannot reach the resonance field, no signal will appear on the screen. If the constant field is increased, a rather broad resonance will start to grow up. When this line has a maximum height, it will start to separate into two lines, the top of each corresponding to the same field.[1] The widths of these lines are smaller than the single line first observed, because of the increasing slope of the sine wave. The true resonance width is computed from the observed line-width, the distance between the peaks and the amplitude of the modulating field.

Fig. 8 shows the proton resonance registered by the recording mA-meter, when the magnetic field has been changed continuously and slowly. The curve in Fig. 8

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[1] A theoretical discussion of the line shape has been given by B. Jacobson and R. Wangsness, Phys. Rev. *73*, 942, 1948.

is of dispersion type. To *localize* resonance lines previously more or less unknown (for subsequent precise measurements) a simple way is obviously to keep the frequency constant and vary the magnetic field if the balance method is used. In view of the very small line-widths, the field has to be changed absolutely continuously over sometimes rather large intervals (if the magnetic moment is not even roughly known). A convenient way to do this is to regulate the cooling water flow, either by shutting it off completely or by diminishing the flow. In this way it was found easy, using the recording mA-meter, to localize resonances. Once these have been found, the precise determination should be made as a direct comparison with one standard nucleus e. g. the proton.

The two-probe arrangement and experimental procedure

Fig. 9 shows a view of the total experimental set up. Two separate complete high frequency bridges were used with a common double beam oscilloscope and one set up for precise frequency measurements. One arm from the bridges contains the sample to be investigated and in one arm of the other bridge is the water sample.

Fig. 10 shows the two probe arrangement. The inner diameters and the lengths of the two coils are exactly equal so that two glass tubes of equal dimensions may be used in the measurements. Only the coils are placed inside the magnet and the remaining parts of the two filters are thus easily accessible for adjustments when balancing the bridges.

If paramagnetic ions were added in order to shorten the relaxation time the same ion concentration in the two equal glass tubes was used. This precaution is taken because of the small increase in the field at the samples due to the paramagnetic effect.

When the two bridges have been adjusted to obtain high sensitivity and amplitude unbalance, the frequencies of the two signal generators are adjusted to such values that the two resonance lines occur on the screen with a minimum of displacement between them.[1] Furthermore the screen is photographed and correction is then made for any small displacement between the lines. A small drift in the magnetic field will now be of less importance, since the two signals will follow each other on the screen, once they have been brought to coincide. The frequency measurements can now be started in accordance with the procedure described below. These measurements were usually repeated, the order of measurement being changed between the two signals. Small drifts of the two frequencies during the times of measurement are of course unavoidable but these drifts could in principle be controlled by observing the line pattern on the screen.

The difference in field between the two places where resonance absorptions were taking place was determined separately by having protons (water) in both coils. The two bridges were fed with the same frequency, and the displacement between the two signals on the screen was measured by photographing the screen pattern. The difference in magnetic field between the two places was then calculated, and turned out to be very small ($\sim 2:10^6$). Correction for this difference can be made when evaluating other magnetic moments.

The frequency measurements were performed in the following way. All signals were compared to a crystal controlled 100 kC Frequency Standard (G. R. 1100-A). The arrangement as a whole can be seen in Fig. 11.

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[1] Each line was then produced in non-split form, according to the middle case in fig. 7.

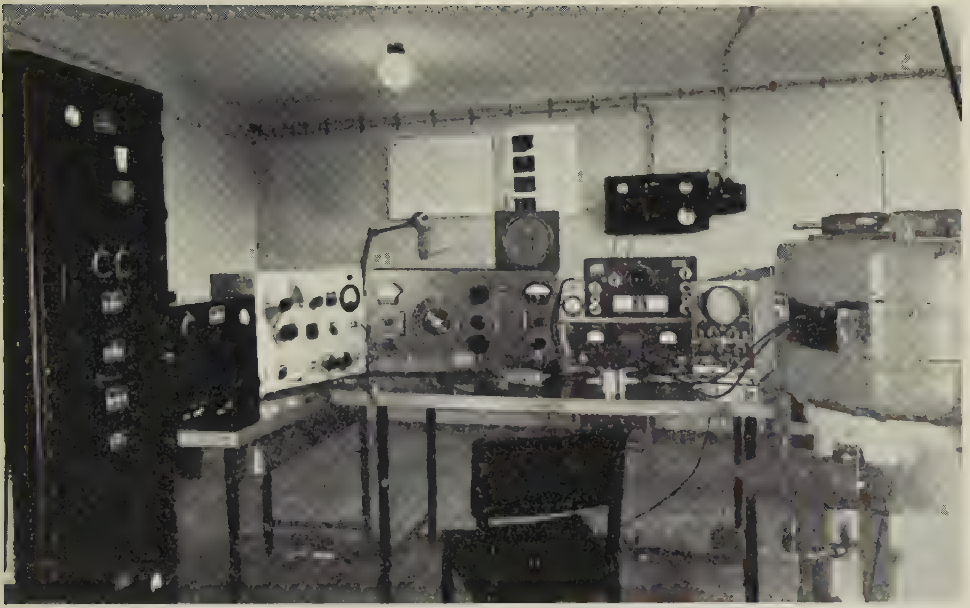

Fig. 9. Total view of the experimental set up.

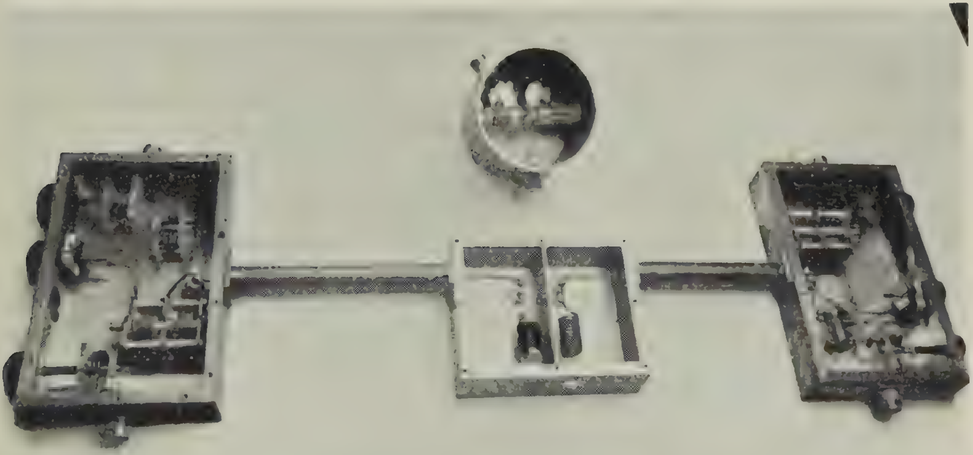

Fig. 10. The two-probe arrangement. The two samples are placed in the coils of the middle box. These coils are connected to two separate h f bridges. In the figure a h f transformer for low frequency is also seen.

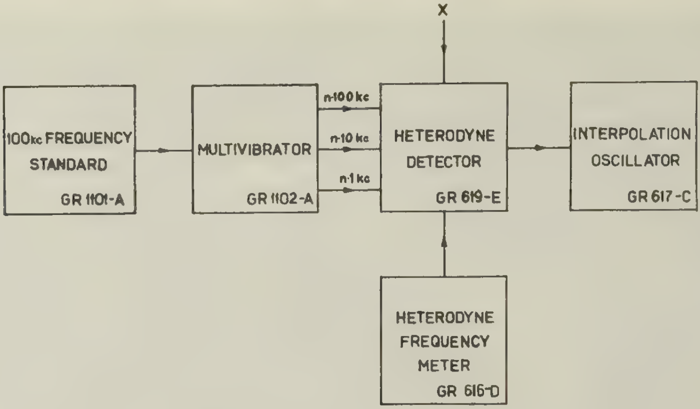

Fig. 11. Block diagram of the h f measuring equipment.

The Heterodyne Detector (G. R. 619 E) is set to audiable beat with the unknown frequency and the Heterodyne Frequency Meter (G. R. 616 D) is connected to the unknown frequency and adjusted to zero beat. These adjustments are made by the three-oscillator method[1] to get as high accuracy as possible. A preliminary value of the frequency is now obtained by adjusting the frequency meter to zero beat with the standard harmonics (($n \cdot 100$ kc) next below and next above the unknown frequency and the preliminary values are then obtained by interpolation. The most accurate value is now obtained by adjusting the frequency meter against the unknown frequency as described above and then beating it with a standard harmonics ($n \cdot 10$ kc). This beat frequency is always ≤ 5 kc and can be measured by the Interpolation Oscillator (G. R. 617-C) which has a frequency range of 0–5 kc and contains an output meter which can be used for zero beat adjustments. The frequency value is obtained by adding or subtracting this value from the standard harmonics ($n \cdot 10$ kc) which best agrees with the preliminary value.

The accuracy of the Interpolation Oscillator is better than ± 1 cycle, but the whole accuracy is limited by the Heterodyne Frequency Meter, which has a frequency range of 100 c–5 000 kc. In this range the accuracy is ± 1 cycle, but if a harmonic is used, for instance the 5th, the meter reading has to be multiplied by 5 and then the accuracy is limited to ± 5 cycles. As mentioned above, in our measurements of nuclear magnetic moments the two frequencies were measured against the same Frequency Standard. To get the ratio of the magnetic moments these frequency values are then divided, which means that the absolute value of the standard frequency will not limit the accuracy. The limitation of accuracy in the frequency measurements would therefore be $\sim 2:10^7$, but it is not possible to make full use of this inherent high accuracy, owing to small drifts in the high frequency generators.

The Results

A. The deuteron to proton ratio

This ratio was determined with the molecular beam resonance method by KELLOG, RABI and RAMSEY[2] and the value obtained by them is 0.30703 ± 0.00010. In connection with a new investigation of the important relation between the magnetic moments of the proton, deuteron and neutron, ARNOLD and ROBERTS[1] for the first time used the new method for precision measurements of these nuclei. They obtained the value $\frac{\mu_D}{\mu_P} = 0.30702 \pm 0.00010$. Thus, in this first investigation the accuracy claimed was not better than the previous one but was anyhow sufficiently good to enable the statement to be made that $\mu_D \neq \mu_P + \mu_n$, since the neutron moment obtained at the same time was much more accurate than had been possible before. Shortly afterwards NAFE, NELSON and RABI[2], when examining the h f s separation of the $^2S_{1/2}$ ground state of hydrogen and deuterium, found a peculiar discrepancy in the value expected from the related ratio of the moments of the deuteron and the proton. ROBERTS[3] therefore repeated his measurements with better technique and obtained a value with much smaller limits of error, namely 0.307002 ± 0.000015. Almost simultaneously BLOCH, LEVINTHAL, and PACKARD[4] published a value considerably more accurate of the deuteron proton ratio, namely $\frac{\mu_D}{\mu_P} = 0.3070126 \pm$ $\pm$ 0.0000020. Finally BITTER, ALPERT, and POSS[5] arrived at the value $\frac{\mu_D}{\mu_P} =$ $=$ 0.307021 ± 0.000005. This value is given with slightly broader margin than the Bloch value, but falls a little outside this value.

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[1] See, for instance, TERMAN: Radio Engineering.

[2] J. M. B. KELLOG, I. I. RABI, and N. F. RAMSEY, Phys. Rev. *56*, 728, 1939.

Using heavy water for the deuteron resonance and the technique described above, we have obtained a value

$$\frac{\mu_D}{\mu_P} = 0.3070183 \pm 0.0000015$$

The investigation was carried out for three different fields, varying considerably among themselves, to see if the ratio was in any way dependent on the absolute value of the fields. No such effect could be observed. The results are summarized in Table I.

Table I.

Magnetic field in Gauss	ν_D in Mc	ν_P in Mc	$\frac{\mu_D}{\mu_P} = \frac{2\,\nu_D}{\nu_P}$
about 3530	2.357340	15.356360	0.3070185
» 5250	3.500000	22.800000	0.3070176
» 5250	3.500000	22.800000	0.3070176
» 5700	3.801091	24.761325	0.3070183
» 5700	3.801073	24.761120	0.3070195
		Mean value	0.3070183
		Maximum error	± 0.0000015

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[1] W. R. ARNOLD and A. ROBERTS, Phys. Rev. *70*, 766, 1946.

[2] J. NAFE, E. NELSON, and I. RABI, Phys. Rev. *71*, 914, 1947. This paper, together with papers by P. KUSCH and E. FOLEY (Phys. Rev. *72*, 1256, 1947 and Phys. Rev. *73*, 412, 1948), initiated also the recent development in quantum electrodynamics especially by J. SCHWINGER (Phys. Rev. *73*, 416, 1948) showing that the Bohr magneton has to be corrected by a factor of 1.0012. See also A. BOHR, Phys. Rev. *73*, 1109, 1948.

[3] A. ROBERTS, Phys. Rev. *72*, 979, 1947.

[4] F. BLOCH, E. C. LEVINTHAL, and M. E. PACKARD, Phys. Rev. *72*, 1125, 1947.

[5] F. BITTER, N. L. ALPERT, and D. E. POSS, Phys. Rev. *72*, 1271, 1947.

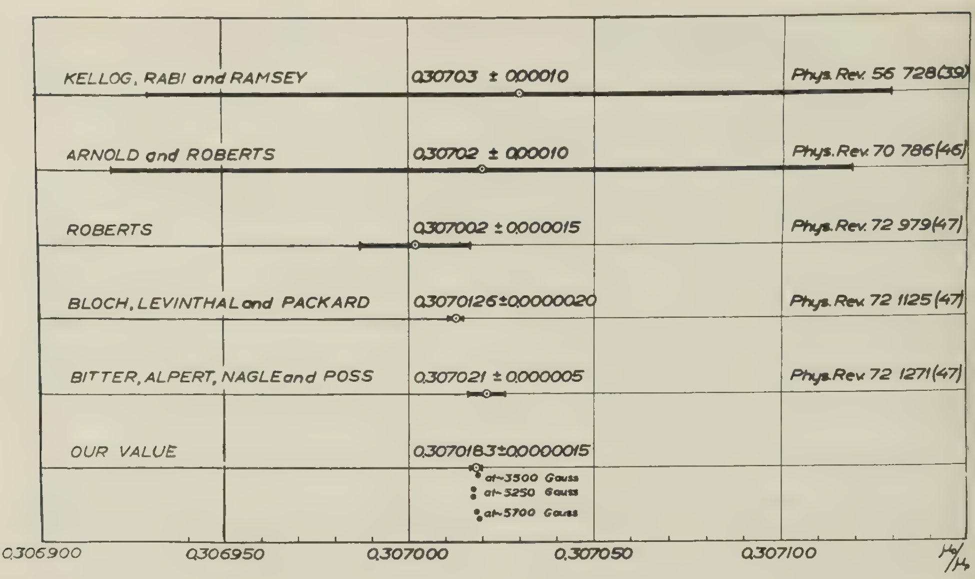

Fig. 12. Diagram, showing the value of μ_D/μ_P hitherto obtained.

At 5250 Gauss, as can be seen in the table, a rather peculiar circumstance made the frequency measurements especially easy to perform. We adjusted one of the generators to a crystal-harmonic (3.5 Mc), and the other generator was adjusted so that the two signals on the screen coincided as near as possible. The frequency of this generator turned out to be very near another crystal-harmonic (22.8 Mc). We repeated this experiment twice and got the same results. Even if these frequency measurements were evidently more easy to perform we have not attached more statistical weight to them than to other measurements in Table I.

The error given in our value is an estimated maximum error, which can be judged from our present knowledge of the factors which seem to limit the accuracy. All our experimental points are well inside these limits. A diagram is given in fig. 12 showing the results hitherto obtained for the ratio $\frac{\mu_D}{\mu_P}$.

As can be seen from this diagram, our value falls inside the limits given by Bitter et al. but is just a little outside the value obtained by Bloch et al. The reason for this very small discrepancy is at the moment hard to find. After all, when considering the very small errors here involved, the mutual agreement between the three last investigations appears at present rather satisfactory.

B. The Li^7 to proton ratio

This ratio has not yet been determined accurately with the new method. The value obtained by MILLMAN and KUSCH[1] with the molecular beam resonance method was $\frac{\mu_{Li^7}}{\mu_P} = 1.16622 \pm 0.00090$.

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[1] S. MILLMAN and P. KUSCH, Phys. Rev. *60*, 91, 1941.

In our experiments the signal to noise ratio of the Li sample was considerably less favourable than in the previous case, and consequently the accuracy could not be made quite as high. The sample consisted of a water solution of $LiNO_3$. The moment was studied for three different fields and no change in the values due to the different fields could be observed in this case either.

The results of the measurements are given in Table II.

Table II.

Magnetic field in Gauss	ν_{Li^7} in Mc	ν_P in Mc	$\frac{\mu_{Li^7}}{\mu_P} = \frac{3\,\nu_{Li^7}}{\nu_P}$
about 5800	9.7249	25.0250	1.16583
» 5900	9.7778	25.1615	1.16581
» 5900	9.7765	25.1575	1.16584
» 5900	9.7776	25.1604	1.16583
» 6810	11.2893	29.0504	1.16583
» 6810	11.2896	29.0501	1.16588
		Mean value	1.16584
		Maximum error	± 0.00004

Thus our new value for the Li^7 magnetic moment is:

$$\frac{\mu_{Li^7}}{\mu_P} = 1.165827 \pm 0.000060$$

C. The F^{19} to proton ratio

The molecular beam resonance method was used by MILLMAN and KUSCH (loc. cit.) to determine the magnetic moment of F^{19}. They obtained the value $\frac{\mu_{F^{19}}}{\mu_P} = 0.9410 \pm 0.0013$. This ratio has not yet been investigated by the new method.

The sample[1] consisted in this case of $C_2F_3Cl_3$ (boiling point = 40° C). The signal to noise ratio was quite sufficient to provide good possibility of accurate measurements.

The measurements were performed for two completely different fields and altogether seven independent points were obtained. The results are given in Table III.

The new value for the magnetic moment of fluorine is then:

$$\frac{\mu_{F^{19}}}{\mu_P} = 0.940334 \pm 0.000015$$

As in the previous cases the limits of error given here are the estimated maximum error and all the individual experimental values fall inside these limits.

In the diagram of Fig. 13 there are plotted the new values for Li^7 and F^{19} and the old values with their limits of error.

The old values are evidently consistent with the new ones when the former's larger limits of error are taken into consideration.

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[1] This sample was kindly given to us by Professor J. TANDBERG.

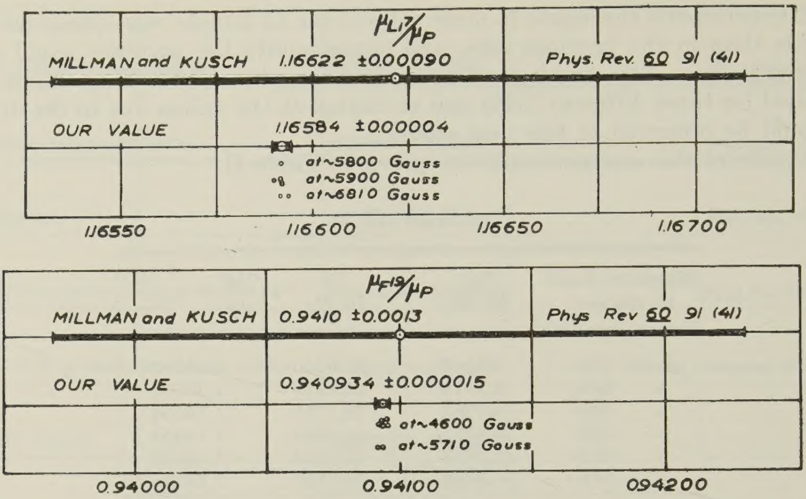

Fig. 13. Diagram showing the values of μ_{Li^7}/μ_P and $\mu_{F^{19}}/\mu_P$ hitherto obtained.

Table III.

Magnetic field in Gauss	$\nu_{F^{19}}$ in Mc	ν_P in Mc	$\frac{\mu_{F^{19}}}{\mu_P} = \frac{\nu_{F^{19}}}{\nu_P}$
about 4600	18.411164	19.566660	0.940946
» 4600	18.414476	19.570116	0.940949
» 4600	18.410958	19.566764	0.940930
» 4600	18.410966	19.566828	0.940927
» 4600	18.410985	19.566736	0.940933
» 5710	22.975250	24.417890	0.940919
» 5710	22.975350	24.417600	0.940934
		Mean value	0.940934
		Maximum error	± 0.000015

The diamagnetic effect

The values for the nuclear magnetic moments given above have not yet been corrected for the diagmagnetic effect. We have preferred to give our values in this uncorrected form since the diamagnetic correction, especially for fluorine (being of higher Z-value), is appreciably greater than the experimental uncertainties themselves. According to present theoretical formulas the correction is not very accurately known either. In fact the accuracy of the present experimental method seems to call for a much more refined theoretical investigation of the diamagnetic effect than has hitherto been necessary.

The theory for the diamagnetic correction to be applied to nuclear magnetic moments was developed by LAMB.[1] This theory has been quite adequate for use in molecular beam resonance investigations. When an external magnetic field is applied, the diamagnetism of the atomic electrons will produce an induced field at the nucleus, the magnitude of which can be computed on using different approximations for the electron wave function. Lamb has shown that, if the Fermi-Thomas model is used, the ratio of the induced field to the external field can be written approximately

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[1] W. LAMB, Phys. Rev. *60*, 817, 1941.

$$\frac{\Delta H}{H} = -\,0.319 \times 10^{-4}\ Z^{4/3}$$

If the Hartree model is used instead, the numerical factor will become smaller (19% for $Z = 19$ and 12% for $Z = 80$).

As an example, the diamagnetic corrections for Li and F according to this treatment are -0.01% and -0.06% respectively. If the Hartree model is used the corrections would be somewhat smaller (for fluorine about 25% less). It is evident that such small corrections are of little significance if the precision in the measurements is of the order of 1‰ or slightly less as in the molecular beam experiments. If the precision is increased to about $1 : 10^5$ as in the new method, the approximations made in the above theoretical treatment may turn out to be inadequate especially for higher Z values, where the absolute magnitude of the correction is increasing.

Another question which has yet to be examined is whether the experimentally measured value of the nuclear magnetic moment may depend to a very small extent on the chemical compound used.

Under all circumstances we find it more correct not to apply any diamagnetic correction yet but to present the experimentally obtained values as they come out from the experiments.

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SUMMARY

1. The new method for measuring nuclear magnetic moments by magnetic resonance absorption is discussed, with references given particularly designed to introduce the reader to different branches where the method has been applied.

2. For precision measurements of nuclear magnetic moments, various requirements have to be imposed on different parts of the apparatus. The importance of a suitable magnetic field is particularly stressed.

3. Special attention has been devoted to forming a very homogeneous field in a moderately sized magnet excited by batteries. A two-probe arrangement is adopted, which permits direct comparison of different nuclear moments with the protons.

4. To compare the different magnetic moments with that of the proton as a unit, the frequencies of the resonance lines expelled on a double beam oscillograph have been measured accurately against a crystal frequency standard.

5. The nuclear magnetic moments of D, Li^7 and F^{19} have been measured and compared with earlier measurements. The results (uncorrected for the diamagnetic effect) are

$$\mu_D/\mu_P = 0.3070183 \pm 0.0000015$$

$$\mu_{Li^7}/\mu_P = 1.165827 \pm 0.000060$$

$$\mu_{F^{19}}/\mu_P = 0.940334 \pm 0.000015$$

6. The diamagnetic correction is discussed.

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